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Development of a DDT Manufacturing and Processing Plant Waste Treatment System

Montrose Chemical Corp of California, Torrance

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16. ABSTRACT The report gives results of a study both to test the feasibility of detoxification of DDT manufacturing wastes, using solvent extraction, and to develop a practical process, if possible. Three different liquid-liquid contacting devices were tested: all provided reasonably good extraction of DDT and homologs from the caustic aqueous phase. Unfortunately, major phase separation problems resulted in excessive losses of monochlorobenzene solvent to the aqueous phase. Efforts to improve coalescence/phase separation were unsuccessful. Further development of a solvent extraction process for detoxification of DDT manufacturing waste cannot be justified.

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by

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ABSTRACT

A process for treating DDT manufacturing waste has been investigated. In this process, concentrated wastes containing a few hundred to a few thousand mg/ℓ of DDT, DDD and DDE as well as tars, ~20% Na_2SO_4, and ~3% sodium p-chlorobenzenesulfonate were extracted in various continous liquid-liquid extractors with monochlorbenzene (MCB) and heptane as extractants.

A primary objective of this study was to determine the existence of a suitable method for making the extraction, and three devices were shown to make good extractions of the caustic waste. The Ross in-line homogenizer and the Podbielniak continuous contactor were both able to reduce the DDT and DDE content to as low as ~2 mg/ℓ, and a baffled turbine mixer in a 3-stage array reduced the DDT + DDE level to as low as 0.2 mg/ℓ.

A second-stage extraction of the aqueous effluent from the Podbielniak unit reduced the DDT content to detection limits, and the DDE to ~0.1 mg/ℓ.

Monochlorbenzene (MCB) has been shown to be a suitable extractant, and appears superior to heptane, used in earlier studies. The use of MCB provides a less flammable solvent, and potentially permits the MCB laden with DDT, DDE to be recycled to process, thus avoiding DDT, DDE disposal by incineration or other processes.

Major problems have occurred relative to adequate phase separation with excessive amounts of solvent being carried over into the aqueous phase. Reasonably good coalescence can be achieved on a glass wool mat, but the treated liquor contains 200 to 4000 mg/ℓ of MCB which is equal or greater to that contained in the untreated waste (reported solubility of MCB in water is 382 mg/ℓ). The formation of emulsions between the aqueous phase and the solvent causes confusion on the efficiency of extraction. The chemical analysis of the aqueous may not be accurate because of the suspended or dissolved MCB in the aqueous phase, which could solubilize DDT and homologs.

Chemical reduction of the MCB was shown to have limited applicability, with six passes through a catalyzed iron reductive column degrading MCB from 225 mg/ℓ to 22 mg/ℓ (90% reduction).

A further problem has been that the densities of the aqueous waste and of MCB are virtually the same, so that gravity separation of the phases is impossible. Dilution of the waste allows phase separation and was used in these studies, but it also requires the treatment of a greater volume of waste.

The cost of an effective, practical process cannot be estimated because the coalescence/phase separation process remains unsolved, as are the methods for removal of residual MCB and sodium salt of monochlorbenzene sulfonic acid (NaMCBS).

The purpose of this study was to determine whether an alternative method to disposal of DDT manufacturing wastes could be developed. The method which was explored was judged to be unworthy of further development.

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Participating from Montrose have been Messrs. Max Sobelman, Vice President - Operations and Grant Director; John Kallok, Plant Manager as Assistant Grant Director; Guy Dimichele, Chemical Engineer; Walter Carey, Chief Control Chemist; Bernard Bratter, DDT Plant Superintendent; and Rick Wilson and Emanuel Moya, Chemical Engineers. The Envirogenics effort was directed by Dr. K. H. Sweeny and carried out by Mr. E. D. Calimag, both under the direct supervision of Dr. C. W. Saltonstall, Jr., Director of Research and Development. The assistance of all participants in the project is appreciated.

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CONTENTS

Abstract ii
Acknowledgment iv
Figures vi
Tables vii

1. Introduction 1
2. Conclusions 4
3. Recommendations 6
4. Podbielniak Continuous Contactor 7

   A. Description of Podbielniak Contactor 7
   B. Experimental Results 7
   C. Summary and Analysis of the Podbielniak Contactor Data 27
   D. Second-Stage Extraction 29

5. Ross In-Line Homogenizer 31

   A. Description of Ross In-Line Homogenizer 31
   B. Experimental Results 31
   C. Summary of Tests With Ross In-Line Homogenizer 58

6. Baffled Stirrers 59

   A. Description of Stirrer System 59
   B. Experimental Results 59
   C. Summary of Baffled Stirrer Tests 63

7. Other Mixing Systems 64

   A. Waring Blendor 64
   B. Ross Laboratory Homogenizer 65
   C. Polytron Homogenizer 65

8. Chemical Reduction of MCB in the Aqueous Extracts 68

9. Analysis of Results 71

References 74

Glossary 75

FIGURES

Number		Page
1	Experimental Setup for Podbielniak Contactor Tests.	8
2	Podbielniak Continuous Contactor	9
3	Ross In-Line Homogenizer	33

TABLES

Number		Page
1	Typical Composition of Waste Discharge to Class I Landfill.	2
2	Analysis of Typical Aqueous Waste.	10
3	Operation of Podbielniak Contactor at 3000 RPM . .	11
4	Operation of Podbielniak Contactor at 4800 RPM . .	11
5	Operation of Podbielniak Contactor at 4800 RPM and 250 mℓ/min MCB Solvent Flow.	12
6	Operation of Podbielniak Contactor at 7000 RPM . .	12
7	Operation of Podbielniak Contactor at 7000 RPM and 2.0:1 Ratio of Waste-to-Solvent Flow	13
8	Operation of Podbielniak Contactor at 7800 RPM and 1.5:1 Ratio of Waste-to-Solvent Flow	14
9	Operation of Podbielniak Contactor at 9500 RPM . .	15
10	Operation of Podbielniak Contactor at 9500 RPM Effect of Increased Outlet Pressure of Waste Flow and Decreased Pressure Solvent Phase	16
11	Operation of Podbielniak Contactor at 9500 RPM 0.3:1 Ratio of Waste-to-Solvent Flow	16
12	Operation of Podbielniak Contactor at 9500 RPM 0.04:1 Ratio of Waste-to-Solvent Flow.	17
13	Operation of Podbielniak Contactor at 9500 RPM 3.0:1 Ratio of Waste-to-Solvent Flow	18
14	Operation of Podbielniak Contactor at 9500 RPM 3.0:1 Ratio of Waste-to-Solvent Flow Effect of Pressure Variations.	18
15	Operation of Podbielniak Contactor at 9450 RPM 4.0:1 Ratio of Waste-to-Solvent Flow	20

TABLES (Cont'd)

Number		Page
16	Operation of Podbielniak Contactor at 9450 RPM 2.8 Ratio of Waste-to-Solvent Flow	21
17	Operation of Podbielniak Contactor at 9450 RPM 3.7:1 Ratio of Waste-to-Solvent Flow	22
18	Operation of Podbielniak Contactor at 9450 RPM 2.5:1 Ratio of Waste-to-Solvent Flow	22
19	Operation of Podbielniak Contactor at 9450 RPM 4.5:1 Ratio Waste-to-Solvent Flow.	23
20	Operation of Podbielniak Contactor at 9450 RPM 4.0:1 Ratio of Waste-to-Solvent Flow	24
21	Operation of Podbielniak Contactor at 9450 RPM 2.0:1 Ratio of Waste-to-Solvent Flow	24
22	Operation of Podbielniak Contactor at 9450 RPM 2.0:1 Ration of Waste-to-Solvent Flow Total Flow 990 m /min.	25
23	Operation of Podbielniak Contactor at 9450 RPM 4.0:1 Ratio of Waste-to-Solvent Flow Total flow 500 mℓ/min.	26
24	Operation of Podbielniak Contactor at 9450 RPM 1.0:1 Ratio of Waste-to-Solvent Flow Total Flow of 500 mℓ/min	26
25	Operation of Podbielniak Contactor at 9450 RPM 1.5:1 Ratio of Waste-to-Solvent Flow Total Flow of 550 mℓ/min	27
26	Summary of Podbielniak Contactor Evaluation Tests.	28
27	Second-Stage Extraction of Podbielniak-Extracted Waste.	30
28	Ross In-Line Homogenizer - Coalescers Evaluated. .	35
29	Ross In-Line Homogenizer Operation - Evaluation of Coalescers.	37

TABLES (Cont'd)

Number		Page
30	Ross In-Line Homogenizer Operation - Effect of Mixing Time on Extraction	38
31	Ross In-Line Homogenizer Operation - Pressure-Aided Flow Through Coalescer	39
32	Ross In-Line Homogenizer Operation - Second-Stage Extraction of Homogenizer - Extracted Waste.	42
33	Operation of Ross In-Line Homogenizer - Effect of Homogenizer Speed of Rotation on Extraction Silicone-Treated Glass Wool Coalescer.	45
34	Operation of Ross In-Line Homogenizer - MCB Recovered When 375 mℓ Mixed with Waste and Passed Through Coalescer	46
35	Effect of Mixing Time on the Extraction With Ross In-Line Homogenizer	47
36	Operation of Ross In-Line Homogenizer Tests With Pressure-Aided (10 psi) Flow Through Coalescer	48
37	Operation of Ross In-Line Homogenizer - Evaluation of Sand and Gravel as Coalescers	50
38	Operation of Ross In-Line Homogenizer - Evaluation of Fine Gravel Coalescer	51
39	Operation of Ross In-Line Homogenizer - Evaluation of Silicone-Treated Sand Coalescer	52
40	Operation of Ross In-Line Homogenizer - Tests With Glass Wool Coalescer.	53
41	Operation of Ross In-Line Homogenizer - Tests With 3 Inch Dia x 30 Inch Deep Glass Wool Coalescer.	54
42	Operation of Ross In-Line Homogenizer - Tests With Pressure-Aided Flow Through Glass Wool Coalescer.	54

TABLES (Cont'd)

Number		Page
43	Operation of Ross In-Line Homogenizer - Second Extraction of Waste With Homogenizer	55
44	Operation of Ross In-Line Homogenizer - Extraction of Waste With Heptane at 7000 RPM.	56
45	Operation of Ross In-Line Homogenizer - Extraction of Waste With Heptane at 10,000 RPM.	57
46	Operation of Ross In-Line Homogenizer - Extraction of Waste With Heptane at 10,000 RPM - Evaluation of Antifoam Agent	57
47	Extraction of Montrose Waste in Baffled Tank Using Straight Blade, Curved Blade and Tapered Blade Turbine Stirrers	60
48	Effect of Blade-Baffle Clearance on Extraction Efficiency - Analysis of Aqueous Phase After Extraction, $\mu g/\ell$	61
49	Multiple Extraction of Montrose Waste With Baffled Straight-Blade Turbine Mixer	62
50	Temperature of Waste-MCB Mix as Function of Mix Time in Waring Blendor	64
51	Extraction Tests With Brinkman Polytron Homogenizer.	66
52	Analysis for Monochlorbenzene DDT and DDE After Treatment in Reduction Column.	69

SECTION 1

INTRODUCTION

The objective of these studies was to investigate a process for the removal of DDT and related products from DDT manufacturing wastes currently discharged to a Class I landfill, and the subsequent treatment or disposal of the removed DDT if necessary. The successful development and demonstration of the subject process would lead to very low discharge of DDT* and related compounds since process recycle previously installed has already eliminated all but the landfilled discharge.

Use of DDT in the U. S. has been eliminated by Federal action, and domestic use is allowed only for emergency situations and under special permit. Examples of such use recently was for control of Bubonic Plague vector in Colorado, and control of the spruce budworm that threatened the forests of the Pacific Northwest.

DDT is still manufactured for export at one plant in the U.S. The majority of exports are made for the purpose of controlling malaria vector in Asia, Africa, Central and South America. Consequently, the only possible release of DDT to the environment in the U.S. could be from the manufacturing process. The manufacturer has taken considerable effort to minimize his water discharges by employing extensive recycle of process water. Thus, the only DDT-containing wastes leaving this plant are approximately 30,000 gallons per day of caustic waste which go to a Class I landfill.

This DDT manufacturing plant makes use of an extensive recycle system which eliminates all but about 2500 gal/day of steam boiler blowdown and sanitary waste. These are discharged to the county sewer. The current operation insures that all government regulations for water standards are being met.

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*DDT + DDD + DDE; see Glossary for definition of terms.

The principal waste discharge to the Class I landfill is neutralized caustic liquor from DDT washing operations, tar pot drainings, spills and tank drainings.[a] The analysis of these wastes is typically shown in Table 1.

TABLE 1

TYPICAL COMPOSITION OF WASTE DISCHARGE
TO CLASS I LANDFILL

Product	Pound/Day
Sodium Sulfate	21,615
Sodium Salt of Monochlorbenzene SulfoniczAcid (NaMCBS)	3,670
Caustic Soda	50
DDT (+ DDE, DDD)	119
Miscellaneous (tars, etc.)	139
Water	255,550
TOTAL	281,143

The total volume of waste may vary somewhat as additional water is added to the landfill discharge. It is this waste for which treatment is considered in this report.

The use of solvents to extract and recover pollutants from waste waters is not a new concept and has been successfully applied on a number of different industrial waste in the extraction of waste water from styrene manufacture; butyl acetate and isopropyl ether for the removal of phenolics in the byproduct coke industry; and 2-ethylhexanol in the removal of ethanol, ethylene dichloride, ethylene chlorohydrin and chloral hydrate from neutralized oxychlorination waste water.

[a]Earhart, J. P., and K. W. Won, et al. University of California, Recovery of Organic Pollutants Via Solvent Extraction. Chemical Engineering Progress, May 1977. pp. 67-73.

Witt and Forbes[a] describe several additional extraction processes successfully employed in the petroleum industry, also noting a few caveats: "This solvent must be inexpensive...(and) it must be almost completely insoluble in water, since the portion that dissolves is lost to the operation and may be a cause of pollution in the water effluent."

Earlier studies under EPA Contract 68-01-0083 (Reference 1) demonstrated that the DDT, DDD and DDE could be effectively removed from the caustic waste provided a high-shear mixing by multiple passage through a centrifugal pump was found effective for DDT removal. Although the principle of high-shear mixing for continuous extraction of DDT mixing process was not considered suitable for ready scale-up to full plant operation.

The primary emphasis of this program was the evaluation of a series of high-shear mixers which could potentially provide a practical means for the requisite high-shear mixing and be readily scaled-up to useful plant treatment capacities. Among the mixing devices considered have been the Podbielniak continuous contactor and several types of continuous and batch-type mixers. Further consideration was given to the solvent employed for the extraction and ultimate disposal systems that could be utilized.

The ultimate disposal of the DDT and DDE could possibly be handled in either of two ways. If a solvent, such as heptane (used in the earlier studies under Contract 68-01-0083, Reference 1), is employed, the removal of the heptane and its return to the system, and a means for disposal of the DDT and DDE must be provided. The heptane can be removed by distillation, and the DDT and DDE in the still bottoms can be destroyed by Friedel-Crafts reaction, incineration, etc. However, a more attractive approach would appear to involve the use of a suitable solvent so that the DDT and DDE can be returned to the process. The use of monochlorbenzene (MCB) as the solvent, with the return of the MCB laden with DDT and DDE to the DDT condensation step of the reaction would eliminate the need for a degradation process to destroy the extracted DDT and DDE, as well as conserving these two materials in the process. Major effort has therefore been directed towards using MCB as the extractant.

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[a]Witt, P.A., Jr., and M. C. Forbes. By-Product Recovery Via Solvent Extraction. Chemical Engineering Process, October 1971. pp. 90-94.

SECTION 2

CONCLUSIONS

It has been demonstrated that high-shear mixing of DDT plant aqueous alkaline waste with monochlorbenzene (MCB) solvent is effective for the extraction of DDT, DDD and DDE from the waste. Levels as low as ~2 mg/ℓ have been obtained (total DDT + DDE) when the Ross homogenizer or Podbielniak contactor are employed, and as low as 0.2 mg/ℓ for a three-stage baffled turbine stirrer. A second-stage extraction (without high-shear mixing) of the Podbielniak-treated waste has reduced the DDT + DDE to 0.1 - 0.2 mg/ℓ. However, the process has not been shown to give adequate coalescense of the phases, so that clear-cut phase separation has not been regularly obtained. Extraction ratios as high as 4 volumes waste/1 volume solvent appear satisfactory for extraction of DDT, DDD and DDE. Of the various high-shear mixers tested, the three-stage baffled stirrer with the 3 inch diameter x 42 inch deep coalescer was the best system.

The wastes were shown to contain ~200 - 1000 mg/ℓ MCB as received and treatment did not reduce, but in some cases (homogenizer) increased, the MCB level, apparently because of ineffective coalescence. Attempted degradation of the MCB by chemical reduction led to regular but slow destruction of the extractant. Six passes through an iron reduction column was necessary for a 90% removal of MCB. The degradation product was cyclohexanol.

The use of MCB as a solvent/extractant is apparently more effective and less flammable than heptane. Use of MCB as the solvent potentially permits recirculation of the extractant to the condensation step of the process so that further disposal process would not be necessary.

It was found that the density of the aqueous waste is regularly equal or nearly equal to MCB. Consequently, dilution of the waste to give a density difference sufficient for gravity separation of the phases is necessary. Such dilution would require the handling and processing of an additional volume of waste.

The less expensive baffled stirrers and in-line homogenizer appeared to function at least as well as the Podbielniak, so that the large capital investment for the continuous contactor is probably not necessary. Cost estimates for an effective practical process cannot be formulated because coalescer and phase separation problems remain unsolved.

SECTION 3

RECOMMENDATIONS

The feasibility of removing DDT and DDE from aqueous DDT manufacturing waste using a high shear mixing solvent extraction process has been demonstrated by tests with the Podbielniak continuous contactor, the Ross In-Line Homogenizer, and baffled turbine stirrers. Reduction in DDT + DDE levels to 0.2 to 2.0 mg/ℓ were regularly obtained. The use of MCB (monochlorbenzene) as a solvent/extractant was deemed attractive because the extracted DDT, DDD and DDE could potentially be returned directly to the process without the added complexity of ultimate disposal of these materials.

However, several serious problems remain. The aqueous raffinate contains 200 to 1000 mg/ℓ of MCB after processing, an amount that is both economically and environmentally not acceptable. Two possibilities exist to remove the MCB from the extracted aqueous waste. Tests with catalytic reduction indicated a reaction rate too slow for practical use. Removal by sorption, either by carbon or macroreticular resins, would be expected to be expensive and difficult because of the viscosity, high solids content, and high amount of materials to be removed from the raffinate. The densities of the waste and the preferred extractant, MCB, are virtually identical so that dilution of the waste is necessary before gravity phase separation can be achieved; this requires handling a larger volume of waste. Further, adequate coalescence and phase separation were not obtained, also leading to excessive and unacceptable MCB loss.

With these factors in mind, it is recommended that scaleup of the process not be attempted.

SECTION 4

PODBIELNIAK CONTINUOUS CONTACTOR

A. Description of Podbielniak Contactor

The Podbielniak contactor is constructed with a series of concentric "bands" perforated with many holes. The unit is rotated at a high speed (up to ~10,000 RPM), and the heavier liquids are thrown outward by centrifugal force, while lighter liquids are displaced inwards. This action causes a series of counter-current contacts as the fluids pass through the perforated bands, thereby producing a multiple stage extraction. Either the heavy or light liquid can be made predominately continuous or dispersed by control of the position of the principal interface; this is done by regulating the pressure on the liquid streams. The centrifugal force (~5000 x g) and the short residence time generally give conditions whereby liquids do not emulsify, effluents are clear and entrainment and settling problems are largely eliminated.

The experimental set-up used in these tests is shown in Figure 1, and a view showing the construction of the Podbielniak contactor is shown in Figure 2.

B. Experimental Results

Two groups of experiments will be described in the section to follow. In the first group, a variety of conditions were explored leading to effective operation of the Podbielniak contactor. In the second group, the operation of the "Pod" at different solvent-to-waste ratios, etc., at the discovered operating conditions is described.

1. Exploratory Runs - Range Finding Experiments

The operating variables for the Podbielniak unit are the input flow rates of the aqueous waste and extractant, the input and output pressure of the heavy and light liquids, and the rate of rotation of the contactor.

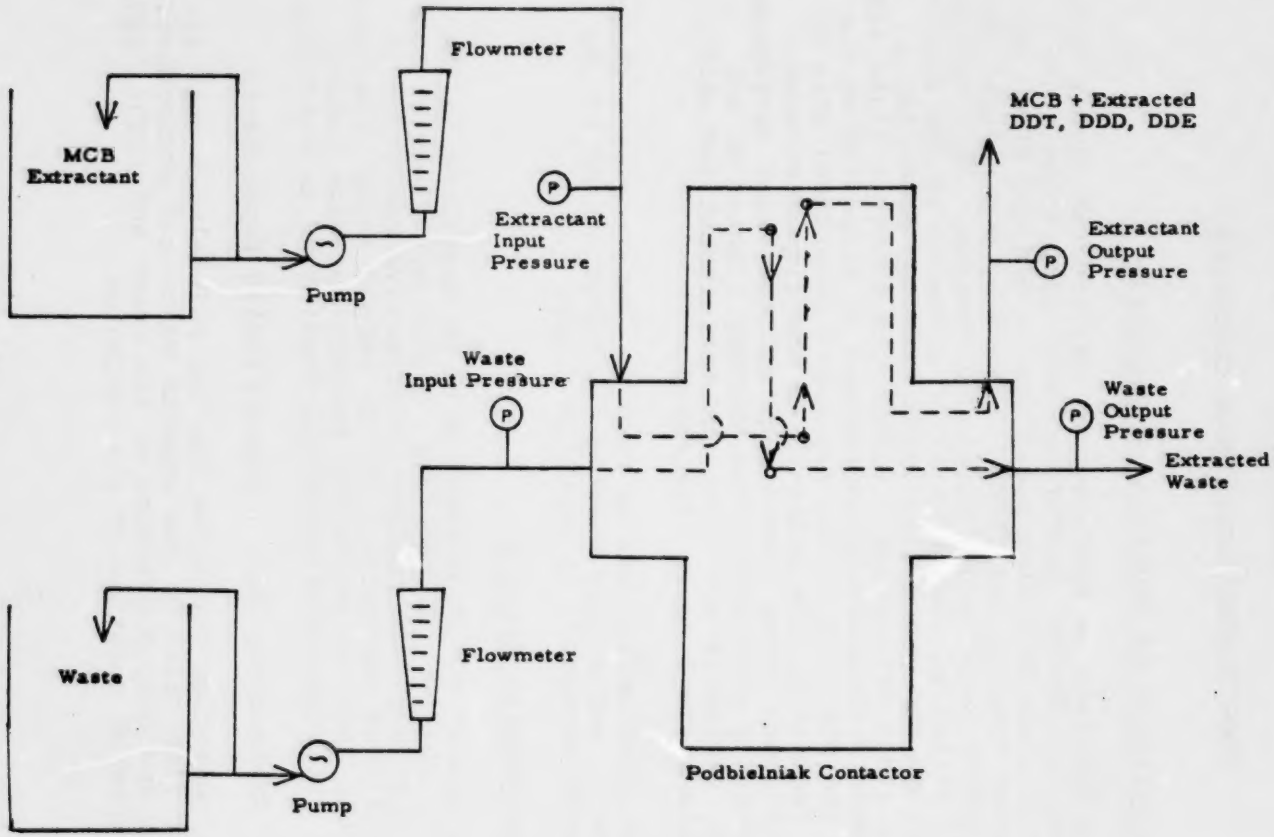

Figure 1. EXPERIMENTAL SETUP FOR PODBIELNIAK CONTACTOR TESTS

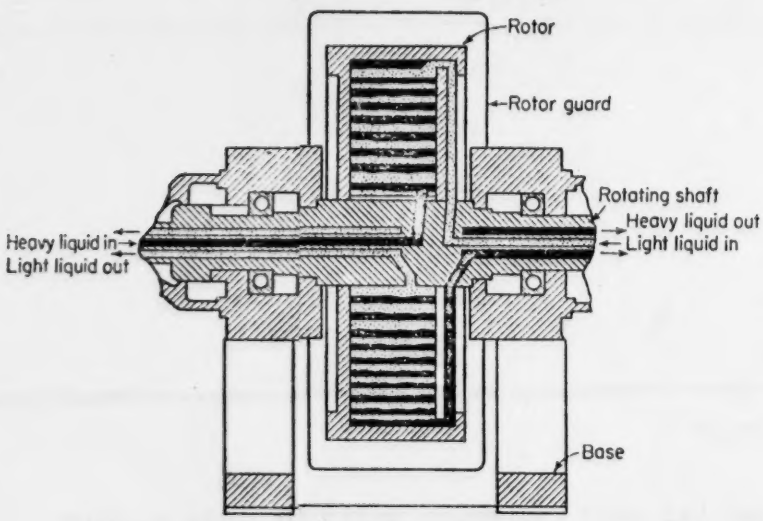

Figure 2. PODBIELNIAK CONTINUOUS CONTACTOR

First Test Series

In the first test series, the waste was diluted to a density of 1.045 while the density of the chlorobenzene (MCB) was 1.096. The densities of the waste and MCB were found to be virtually identical when the waste was undiluted. The analysis of a typical waste sample is shown in Table 2.

TABLE 2

ANALYSIS OF TYPICAL AQUEOUS WASTE*

	Analysis, mg/ℓ
p,p'-DDT	56
o,p'-DDT	14
p,p'-DDE	73
o,p'-DDE	18
chlorobenzene	410
density, g/mℓ	1.045

*Diluted for test

In the initial test, aqueous waste at 1690 m /min at a pressure of 10 psig, and MCB at 200 mℓ/min were fed to the contactor. The outlet valves were opened to give zero pressure for both phases, and the contactor was rotated at 3000 RPM. No clear separation of phases was obtained, with both layers being dark colored. The analysis of the phases gave the results as shown in Table 3.

TABLE 3

OPERATION OF PODBIELNIAK CONTACTOR AT 3000 RPM

	ANALYSIS, mg/ℓ	
	Aqueous Phase	Solvent Phase
p,p'-DDE	75.2	39.7
o,p'-DDE	36.7	11.5
p,p'-DDD	--	--
p,p'-DDT	180.0	--
o,p'-DDT	125.0	132.0

The extraction was poor, probably because a clear separation of phases was not obtained.

In the second test, the rate of rotation of the contactor was increased to 4800 RPM, and the inlet pressure of the aqueous phase increased to 20 psig (flow rate 3808 mℓ/min). Again no clear separation of phases was obtained, and the extraction efficiency was similar to the first test. The results are shown in Table 4.

TABLE 4

OPERATION OF PODBIELNIAK CONTACTOR AT 4800 RPM

	ANALYSIS, mg/ℓ	
	Aqueous Phase	Solvent Phase
p,p'-DDE	72.4	65.2
o,p'-DDE	32.1	28.5
p,p'-DDD	--	--
p,p'-DDT	66.7	13.3
o,p'-DDT	110.0	147.0

In the third test, the solvent flow was increased to ~250 mℓ/min, and the output pressure increased from a nominal 0 psi to 1.0 psig. Other conditions were the same. In this test, a clear separation of phases was obtained, but analyses of the phases did not show appreciably better extraction. The analyses are shown in Table 5.

TABLE 5

OPERATION OF PODBIELNIAK CONTACTOR AT 4800 RPM AND 250 mℓ/min MCB SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Phase
p,p'-DDE	44.0	64.5
o,p'-DDE	11.2	24.3
p,p'-DDD	--	--
p,p'-DDT	133.0	--
o,p'-DDT	96.8	76.1

Following this, the speed of rotation of the contactor was increased from 4800 to 7800 RPM. The other conditions remained the same, except that the flow rate of the aqueous waste decreased from 3800 mℓ/min to 1674 mℓ/min. A clear separation of phases was obtained, and substantially better extraction was shown. The analyses are shown in Table 6.

TABLE 6

OPERATION OF PODBIELNIAK CONTACTOR AT 7000 RPM

	ANALYSIS, mg/ℓ	
	Aqueous Phase	Solvent Phase
p,p'-DDE	59.3	72.1
o,p'-DDE	26.1	36.6
p,p'-DDD	23.3	--
p,p'-DDT	--	133.0
o,p'-DDT	--	110.0

In the next test, the solvent flow rate was 822 mℓ/min, while the solvent pressure was 20 psig input and output, and the waste 35 psig input and 5 psig output. In this test, a clear separation of phases was not obtained.

The aqueous phase effluent contained about 50% solvent phase and the MCB solvent phase contained about 10% aqueous phase. In this test, and succeeding tests, there was no sharp separation of phases, but the MCB outlet would have some aqueous phase which separated rapidly, and the aqueous waste outlet some MCB which separated quickly. Large-scale operation of the Podbielniak would appear to require a continuous decanter to separate the phase in both the heavy and light liquid outlet streams, though it is possible that with fine tuning, a larger unit may provide better separation. The phases were allowed to separate and the layers tested. The analyses showed about 98% extraction. The results are shown in Table 7.

TABLE 7

OPERATION OF PODBIELNIAK CONTACTOR AT 7000 RPM AND 2.0:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	2.5	20.5
o,p'-DDE	0.5	54.5
p,p'-DDD	- -	- -
p,p'-DDT	- -	87.0
o,p'-DDT	- -	21.0

This test showed good extraction after the separation of phases, with no detected DDT or DDD, and only 3 mg/ℓ of the DDE isomers.

As a further test, the flow rate of the aqueous phase was reducted from 1865 to 1234 mℓ/min, the inlet pressure of the MCB solvent increased from 20 to 25 psig, the outlet pressure increased from 20 to 35 psig, the inlet pressure of the aqueous phase increased from 35 to 50 psig. The rate of flow of the MCB solvent remained at 822 mℓ/min, and the speed of rotation 7800 RPM. The results of this test are shown in Table 8.

TABLE 8

OPERATION OF PODBIELNIAK CONTACTOR AT 7800 RPM AND 1.5:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	1.0	40.0
o,p'-DDE	--	7.5
p,p'-DDD	--	--
p,p'-DDT	--	16.5
o,p'-DDT	--	4.5

In this test, the aqueous phase contained about 30% MCB (after phase separation), while the solvent stream appeared to be free of the aqueous phase.

At this point, a pressure regulator was installed in the solvent effluent stream, the rate of rotation of the contactor increased from 7800 to 9500 RPM (full-speed), and the pressures adjusted on the basis of the manufacturer's recommendations for the phase densities and speed of rotation. These values were: aqueous phase input 35 psig, output 10.7 psig; and MCB solvent 35 psig input and 20 psig output. In this test, both output streams were about 50% solvent, 50% aqueous. The analysis of the separated phases is as shown in Table 9.

TABLE 9

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 RPM

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	44.5	31.5
o,p'-DDE	6.5	3.5
p,p'-DDD	--	--
p,p'-DDT	62.0	11.5
o,p'-DDT	13.0	3.5

The extraction was not effective, and indeed, there was apparently more of the DDE and DDT in the aqueous layer than in the solvent phase. This anomalous result is probably due to solvent carry-over into the aqueous phase.

In the next test, the outlet pressure on the aqueous phase was increased from 10.7 to 20 psig, while the input pressure remained 35 psig; and the inlet pressure for the solvent phase was decreased from 35 to 20 psig, and the outlet pressure decreased from 20 psig to zero psig. Other conditions remained the same. In this experiment, the light phase output, which should have been the extracted aqueous phase was MCB solvent, and the supposed heavy phase was the less dense aqueous phase. The analysis of the phases is shown in Table 10.

TABLE 10

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 RPM
EFFECT OF INCREASED OUTLET PRESSURE OF
WASTE FLOW AND DECREASED PRESSURE SOLVENT PHASE

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	3.5	90.5
o,p'-DDE	--	32.5
p,p'-DDD	--	--
p,p'-DDT	--	100.0
o,p'-DDT	--	20.0

Prior to the next test, a back-pressure valve was installed in the aqueous discharge line, the MCB solvent flow was adjusted to 2500 mℓ/min, and the aqueous flow to 702 mℓ/min. The MCB solvent inlet pressure was 60 psig, while the outlet pressure was 40 psig and the aqueous phase 60 psig inlet and 30 psig outlet. Other conditions were the same as previously. The analyses are as shown in Table 11.

TABLE 11

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 RPM
0.3:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	73.5	76.5
o,p'-DDE	13.5	47.5
p,p'-DDD	--	--
p,p'-DDT	172.0	144.0
o,p'-DDT	62.0	32.0

Despite the high ratio of solvent-to-aqueous waste, the extraction was poor. In this test, the "heavy" phase contained about 80% aqueous phase (should have been all MCB) and the "aqueous" outlet phase contained about 60% MCB.

The ratio of solvent to aqueous waste was further increased in the next test to 8000 mℓ/min MCB extractant and 308 mℓ/min aqueous phase. The MCB inlet pressure was decreased from 60 psig to 40 psig, while the outlet pressure of the MCB was decreased from 40 to 10 psig and the aqueous outlet from 30 to 20 psig. In this test the "aqueous" outlet contained about 98% solvent and the "solvent" outlet 60% aqueous waste. The analysis of the phases again indicated a poor extraction. The results are shown in Table 12.

TABLE 12

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 RPM
0.04:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	61.5	83.5
o,p'-DDE	8.0	30.0
p,p'-DDD	--	--
p,p'-DDT	184.0	170.0
o,p'-DDT	66.0	48.0

Changing the ratio of aqueous waste to solvent to 3.0:1 (3300 mℓ/min aqueous waste, 100 mℓ/min MCB solvent), and the pressures to MCB:inlet 20 psig, outlet 40 psig; aqueous waste:inlet 45 psig, outlet 10 psig, led to an effluent of which the solvent phase appeared free of aqueous waste, and the aqueous waste contained only about 10% MCB. However, the extraction was still poor, probably because of the solvent remaining in the aqueous phase. The results are as shown in Table 13.

TABLE 13

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 PRM
3.0:1 RATIO OF WASTE-TO-SOLVENT FLOW

	AQUEOUS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	72.5	49.5
o,p'-DDE	49.0	49.9
p,p'-DDD	--	--
p,p'-DDT	148.0	23.5
o,p'-DDT	26.5	5.0

In two additional tests, an adjustment of the pressures did not lead to significantly improved results, nor a clear separation of the phases. The test conditions and the results of these tests are as shown in Table 14.

TABLE 14

OPERATION OF PODBIELNIAK CONTACTOR AT 9500 RPM
3.0:1 RATIO OF WASTE-TO-SOLVENT FLOW
EFFECT OF PRESSURE VARIATIONS

TEST CONDITIONS	1st Test	2nd Test
Aqueous Waste Flow, mℓ/min	3300	3300
MCB Solvent Flow, mℓ/min	1100	1100
Aqueous Waste Pressure, psig		
Inlet	50	50
Outlet	20	~0
MCB Solvent Pressure, psig		
Inlet	50	50
Outlet	30	30

(Continued)

TABLE 14 (Continued)

	ANALYSIS, mg/ℓ			
	1st Test		2nd Test	
	Aq	MCB	Aq	MCB
p,p'-DDE	3.5	80.5	5.0	84.5
o,p'-DDE	30.0	17.5	--	--
p,p'-DDD	--	--	--	--
p,p'-DDT	168.0	121.0	56.0	104.0
o,p'-DDT	49.5	25.5	9.5	24.5

Second Test Series

At this point, several changes were made in the procedure and method of operation, and significant improvement is phase separation and extraction efficiency was obtained. These changes included a shortening of the piping to provide reduced resistance, particularly for the outlet pressures; use of damped pressure gauges and lower range flowmeters for more accurate measurement and control of these variables; and starting the contactor with solvent before turning on the aqueous waste pump, rather than starting the flows simultaneously.

The first test with the revised apparatus was made with an aqueous waste flow rate of 800 mℓ/min and a MCB solvent flow of 200 mℓ/min. The solvent and aqueous waste inlet pressures were 13 psig, while the outlet pressures were ~0 psig. The rate of rotation of the contactor was 9450 RPM. The results of this test are as shown in Table 15.

TABLE 15

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
4.0:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	5.5	57.0
o,p'-DDE	1.0	19.5
p,p'-DDD	--	--
p,p'-DDT	--	98.5
o,p'-DDT	--	30.0

Even though the aqueous phase outlet contained about 20% MCB after phase separation, the analysis of the aqueous layer indicated good extraction of DDT and homologs. The efficiency of extraction was 97.0%. As was explained earlier, phase separation of MCB from aqueous layer appears to take place quickly, but the aqueous outlet generally contains an MCB layer, and the MCB outlet an aqueous layer which must be separated before analysis.

Evaluation Tests

With the results shown in the previous test, further tests were made to confirm these findings, and to investigate the effect of solvent-to-waste flow ratio and total flow.

In the first of these evaluation tests, the inlet and outlet pressures remianed the same; and the flow of aqueous waste was 453 m*l*/min, with solvent flow at 160 m*l*/min, giving a waste-to-solvent ratio of 2.8:1. In this test, the aqueous waste raffinate contained about 15% solvent, and the solvent effluent about 3% aqueous waste. The results are as shown in Table 16.

TABLE 16

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
2.8 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	3.5	39.0
o,p'-DDE	0.2	13.5
p,p'-DDD	--	--
p,p'-DDT	--	105.5
o,p'-DDT	--	21.5

The DDT isomers and DDD appear to be extracted more efficiently than DDE (both isomers). This difference is believed to be due to the greater solubility of DDE in water.

The extraction efficiency was 98.0% in this test, with the DDE isomers analyzing 3.7 mg/ℓ and the DDT and DDD undetected in the aqueous effluent.

In another test, a flow rate of 563 mℓ/min of aqueous waste and 151 mℓ/min of MCB solvent was used, giving a waste-to-solvent ratio of 3.73. In this experiment, the aqueous output contained about 13% MCB, and the solvent outlet 2% aqueous waste. The extraction was again effective, with an extraction efficiency of 98.0%. The results are as shown in Table 17.

TABLE 17

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
3.7:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	3.0	44.5
o,p'-DDE	1.0	10.0
p,p'-DDD	--	--
p,p'-DDT	--	112.5
o,p'-DDT	--	25.0

In a further test, a flow rate of 500 mℓ/min of aqueous waste and 200 mℓ/min of MCB solvent was employed (waste-to-solvent ratio 2.5) with the inlet pressure (both fluid streams) at 12 psig. The extraction was not as effective as the previous tests. Extraction efficiency was 94.4%. The results are as shown in Table 18.

TABLE 18

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
2.5:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	7.0	44.5
o,p'-DDE	1.5	12.5
p,p'-DDD	--	--
p,p'-DDT	2.5	125.0
o,p'-DDT	1.5	28.0

The ratio of aqueous waste-to-solvent was increased to 4.5 in the next test, in which the MCB solvent flow rate remained at 200 mℓ/min, while the aqueous waste flow rate was increased to 900 mℓ/min. A 97.4% extraction efficiency was obtained. The results are as shown in Table 19.

TABLE 19

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
4.5:1 RATIO WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	3.5	51.0
o,p'-DDE	1.0	12.0
p,p'-DDD	--	--
p,p'-DDT	1.0	120.0
o,p'-DDT	0.35	35.0

The ratio of aqueous waste to solvent was adjusted to 4.0 in a test in which 800 mℓ/min of the aqueous waste was extracted with 200 mℓ/min of MCB solvent. The aqueous waste effluent stream contained about 18% MCB, while the solvent stream appeared to be free of the aqueous waste. Extraction was excellent, with a 99.5% extraction efficiency, and only 0.6 mg/ℓ of p,p'-DDE detected in the extracted waste stream. The results are as shown in Table 20.

TABLE 20

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
4.0:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	0.6	44.0
o,p'-DDE	--	9.0
p,p'-DDD	--	--
p,p'-DDT	--	55.0
o,p'-DDT	--	16.0

The aqueous waste-to-solvent ratio was adjusted to 2.0 in the next test, with an aqueous waste flow rate of 1000 mℓ/min, and the MCB solvent flow rate 500 mℓ/min. In this test the inlet pressure of the solvent was increased from 14 to 18 psig, and the aqueous waste to 16 psig. The effluent aqueous waste contained about 27% MCB, while the solvent stream contained is less than 1% of aqueous waste. Again, the extraction was excellent, with only 1.0 mg/ℓ of p,p'-DDE in the extracted waste and a 99.1% extraction efficiency. The results are as shown in Table 21.

TABLE 21

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
2.0:1 RATIO OF WASTE-TO-SOLVENT FLOW

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	1.0	37.0
o,p'-DDE	--	9.0
p,p'-DDD	--	--
p,p'-DDT	--	55.0
o,p-DDT	--	13.0

The efficiency of extraction was next investigated at the same 2:1 aqueous waste to MCB solvent flow rate, but with the total flow reduced from 1500 mℓ/min to 990 mℓ/min. In this test the aqueous waste feed rate was 660 mℓ/min, and the MCB solvent was fed to the contactor at 330 mℓ/min. The pressure for the two inlet streams (waste and solvent) was 15 psig. In this test, the aqueous effluent stream contained about 34% MCB solvent while the solvent stream appeared to be clear of aqueous waste. The results of this test indicate a 94.[illegible]% extraction efficiency. The results are as shown in Table 22.

TABLE 22

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
2.0:1 RATIO OF WASTE-TO-SOLVENT FLOW
TOTAL FLOW 990 mℓ/min

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	1.0	26.5
o,p'-DDE	0.35	7.0
p,p'-DDD	--	--
p,p'-DDT	0.15	9.0
o,p'-DDT	1.0	4.5

In the next test, the aqueous waste-to-solvent flow was increased to 4.0, with 400 mℓ/min aqueous waste and 100 mℓ/min MCB solvent, for a combined total flow of 500 mℓ/min. The results did not produce satisfactory extraction, possibly because of the low solvent flow rate. The extraction efficiency was 78.1%. The aqueous effluent appeared to contain no MCB, and the solvent stream had about 1% aqueous phase in it. The analysis is as shown in Table 23.

TABLE 23

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
4.0:1 RATIO OF WASTE-TO-SOLVENT FLOW
TOTAL FLOW 500 mℓ/min

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	34.5	81.0
o,p'-DDE	10.5	42.0
p,p'-DDD	--	--
p,p'-DDT	17.0	92.0
o,p'-DDT	7.5	33.0

Equal quantities of solvent and aqueous waste (250 mℓ/min) were used in the next test, for a combined flow rate of 500 mℓ/min. Pressures of 17 psig on the solvent stream and 7 psig on the aqueous waste inlet stream were required. Both the solvent stream and aqueous effluent appeared to be clear of the other phase. The extraction efficiency was 82.1%. The results are as shown in Table 24.

TABLE 24

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
1.0:1 RATIO OF WASTE-TO-SOLVENT FLOW
TOTAL FLOW OF 500 mℓ/min

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	9.5	24.0
o,p'-DDE	2.5	6.5
p,p'-DDD	--	--
p,p'-DDT	2.0	31.5
o,p'-DDT	1.5	9.0

The ratio of waste to solvent was increased to 1.5 in a test in which 300 mℓ/min of the aqueous waste and 200 mℓ/min of MCB solvent were employed. The extraction efficiency in this experiement was 95.4%. The results of the analysis of the separated phases are as shown in Table 25.

TABLE 25

OPERATION OF PODBIELNIAK CONTACTOR AT 9450 RPM
1.5:1 RATIO OF WASTE-TO-SOLVENT FLOW
TOTAL FLOW OF 550 mℓ/min

	ANALYSIS, mg/ℓ	
	Aqueous Phase	MCB Solvent
p,p'-DDE	5.0	49.0
o,p'-DDE	1.0	12.0
p,p'-DDD	--	--
p,p'-DDT	0.50	64.5
o,p'-DDT	0.35	18.0

It was intended that tests also be made with a hydrocarbon solvent as a comparison with the chlorinated MCB. However, the contactor in operation heated to about 60°C, and it was not considered advisable to use a flammable solvent, such as heptane, under these conditions.

C. Summary and Analysis of the Podbielniak Contactor Data

The Podbielniak contactor was shown to be effective for the extraction of aqueous DDT plant waste with monochlorbenzene (MCB) extractant under defined conditions. Data summarizing a series of evaluation runs are as shown in Table 26.

TABLE 26

SUMMARY OF PODBIELNIAK CONTACTOR EVALUATION TESTS

Ratio Aq. Waste/ MCB	Flow, mℓ/min			Aqueous Effluent Analysis, mg/ℓ					Exten. Efficiency %
	Aq. Waste	MCB	Total	p,p'-DDE	o,p'-DDE	p,p'-DDT	o,p'-DDT	Total	
1.0	250	250	500	9.5	2.5	2.0	1.5	15.5	82.1
1.5	300	200	500	5.0	1.0	0.50	0.35	6.85	95.4
2.0	660	330	990	1.0	0.35	0.15	1.0	2.5	94.9
2.0	1000	500	1500	1.0	0	0	0	1.0	99.1
2.5	500	200	700	7.0	1.5	2.5	1.5	12.5	94.4
2.8	453	160	613	3.5	0.2	0	0	3.7	98.0
3.73	563	151	714	3.0	1.0	0	0	4.0	98.0
4.0	400	100	500	34.5	10.5	17.0	7.5	69.5	78.1
4.0	800	200	1000	0.6	0	0	0	0.6	99.5
4.0	800	200	1000	5.5	1.0	0	0	6.5	97.0
4.5	900	200	1100	3.5	1.0	1.0	0.35	5.85	97.4

From this tabulation, it appears that greater than 95% extraction will be obtained with maximum rate of contactor rotation, a waste-to-solvent flow rate of 1.5 to 4.5, and a total flow of 500 to 1500 mℓ/min; the only very poor extraction was achieved when only 100 mℓ/min solvent was employed (aqueous waste 400 mℓ/min, total flow 500 mℓ/min).

As stated earlier, in a number of the tests, a small to moderate quantity of MCB solvent was found in the aqueous stream, or aqueous waste in the solvent stream, but the phases separated rapidly, and possibly clean layers could be obtained in a larger operation with continuous decanters.

In summary, the Podbielniak continuous contactor appears capable of giving greater than 95% extraction of the DDT, DDD and DDE from aqueous alkaline waste, to give an aqueous phase generally with 5 mg/ℓ or less pesticide components. Waste to solvent ratios of ~4:1 and flows of 1-1.5 ℓ/min appear satisfactory. No evidence of phase emulsification was seen, though the conditions of operation to give a waste stream without significant MCB entrainment appear to be very narrow; that is, the operation of the unit must be carefully controlled if, indeed, it is possible to keep MCB to a practical minimum. Except for this problem of solvent entrainment in the aqueous layer, the Podbielniak under very carefully controlled conditions, was shown to give effective extraction of the DDT from Montrose waste -- but still not good enough to permit discharge of the treated aqueous waste to the public server.

D. "Second-Stage" Extraction

Earlier work carried out under EPA Contract 68-01-0083 (Reference 1) showed that the levels of DDT, DDD and DDE could be substantially reduced from ~10 - 20 mg/ℓ to a few μg/ℓ by a further extraction of the samples, following the initial high-shear mixing. This concept has been further examined with the extraction of aqueous effluent from the Podbielniak contactor.

In these tests, the aqueous effluent was shaken for one minute with 1/4 its volume of MCB solvent, and the separated layers analyzed. This process was repeated with the aqueous layer from the above extraction, if any pesticides remained after the first extraction. This test was carried out with the aqueous effluent from the preceding six Podbielniak contactor runs. The results of the tests are as shown in Table 27.

TABLE 27

"SECOND-STAGE" EXTRACTION OF PODBIELNIAK-EXTRACTED WASTE

		ANALYSIS OF AQUEOUS PHASES, mg/ℓ *				
		p,p'-DDE	o,p'-DDE	p,p'-DDD	p,p'-DDT	o,p'-DDT
1.	Pod Effluent**	0.6	~0	~0	~0	~0
	1st Extn	~0	~0	~0	~0	~0
2.	Pod Effluent	1.0	~0	~0	~0	~0
	1st Extn	~0	~0	~0	~0	~0
3.	Pod Effluent	1.0	0.35	~0	0.15	1.0
	1st Extn	~0	~0	~0	~0	~0
4.	Pod Effluent	34.5	10.5	~0	17.0	7.5
	1st Extn	2.0	0.65	~0	0.6	0.8
	2nd Extn	0.35	~0	~0	~0	~0
5.	Pod Effluent	9.5	2.5	~0	2.0	1.5
	1st Extn	~0	~0	~0	~0	~0
6.	Pod Effluent	5.0	1.0	~0	0.50	0.34
	1st Extn	0.4	~0	~0	~0	~0
	2nd Extn	0.2	~0	~0	~0	~0

* Approximate Sensitivity Limits: p,p'-DDE 0.25 μg/ℓ ; o,p'-DDE 0.33 μg/ℓ ; p,p'-DDD 0.38 μg/ℓ ; p,p'-DDT 0.37 μg/ℓ ; o,p'-DDT 0.41 μg/ℓ .

**The samples labeled "Pod Effluent" give the analysis of the aqueous phase exiting the Pod and represents the input to the "second-stage" extraction.

SECTION 5

ROSS IN-LINE HOMOGENIZER

A. Description of Ross In-Line Homogenizer

The Ross homogenizer was selected for tests as a good representative of the various high shear emulsifiers and homogenizers which are available. The mixing head consists of a 1-3/8 inch diameter set of four blades rotating within a closely fitting "stator." The slotted stator, giving the highest shear, has been used in these tests. The speed of rotation of the blades can be varied up to 10,000 RPM. The rotation of the rotor within the stator gives a flow pattern wherein the fluid is pulled into the cavity of the rotor and forced out through the slots in the stator. For the in-line model, the mixing head is enclosed so that fluid is drawn into the rotor cavity and expelled radially after passing the stator assembly. The pumping and mixing action of the homogenizer is thus broadly similar to the action of a centrifugal pump, (which had been found useful for mixing in earlier studies.) A schematic view of the Ross homogenizer is shown in Figure 3.

In operation, the solvent and waste streams were pumped into the vessel in which the in-line homogenizer was contained and were mixed before entering the homogenizer. The mixed phases then passed through the homogenizer and gave phases which separated slowly. The stream then was passed into a coalescer and continuous decanter from which samples were withdrawn periodically.

B. Experimental Results

The operation of the Ross homogenizer followed earlier experience (Section 7) using the laboratory model of the device. (The in-line model was not yet available.) This experience showed the need for (1) mixing at or near the highest speeds, and (2) a coalescer appeared necessary for adequate separation of phases.

These data show that effluent from the Podbielniak contactor containing 0.6 to 15.5 mg/ℓ of DDT, DDD, and DDE were reduced to detection limits (0.1-0.2 μg/ℓ) when extracted one additional time with MCB solvent. In an additional test in which 69.5 mg/ℓ of the combined toxicants were present, the level was reduced to 4.05 mg/ℓ by the first extraction and 0.35 mg/ℓ by a second extraction of the aqueous phase. In another test, Podbielniak effluent assaying 6.85 mg/ℓ was reduced to 0.4 mg/ℓ by the first extraction and 0.2 mg/ℓ by an additional extract. These data show clearly that a second-stage extraction of the Podbielniak contactor effluent, as could be achieved with a packed tower, would appear to reduce the toxicants to detection limits (~0.1 μg/ℓ). There appears to be no need for high-shear mixing in the second-stage extraction if the mixing is adequate in the first stage of the extraction process.

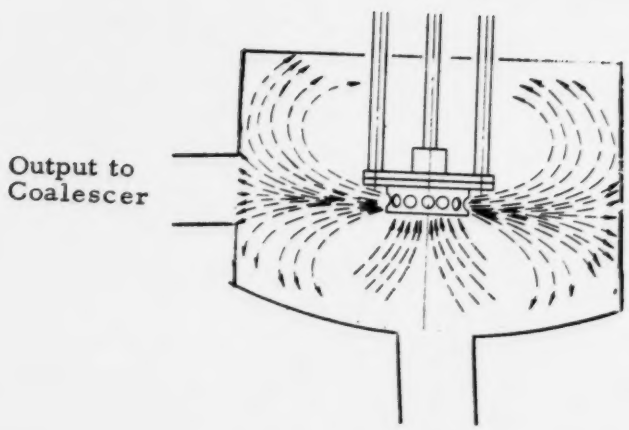

Figure 3. ROSS IN-LINE HOMOGENIZER

In initial experiments, the Ross was operated at 9000 RPM with four volumes of waste (diluted to density of 1.015) to one volume of monochlorbenzene (MCB) extractant. The purpose of these experiments was to evaluate several types of coalescers so as to determine a possible configuration giving adequate phase separation after mixing; the mixer can be evaluated adequately only if the phases can be completely separated after the high shear mixing.

Data from the tests are shown in Table 28.

TABLE 28

ROSS IN-LINE HOMOGENIZER OPERATION - COALESCERS EVALUATED

	COALESCER TESTS		
	Coalescer Material	Observation	Extraction Efficiency, %
1.	No coalescer	Two layers but no clear MCB separation	93
2.	Glass Wool 1.5" dia x 6" deep	Two layers but no clear MCB separation	96
3.	Glass Wool + "Scotchguard"* 1.5" dia x 6" deep	Two layers formed, slow flow through coalescer	92
4.	Cotton + "Scotch-guard" 1.5" dia x 6" deep	Two layers formed. Very slow flow through coalescer	80
5.	Cotton 1.5" dia x 6" deep	Two layers formed. Very slow flow through coalescer	93
6.	Fritted glass	Two layers formed but no clean MCB separation	96

*A silicone producing a hydrophobic coating; a product of 3M Company.

The total DDT + DDD + DDE in the aqueous extracted material under the best conditions was about 2.6 mg/ℓ, or generally equivalent to the results with the Podbielniak contactor described earlier. The analyses of the aqueous layer from the preceding tests are shown in Table 29.

TABLE 29

ROSS IN-LINE HOMOGENIZER OPERATION - EVALUATION OF COALESCERS

	Coalescer Material	Analysis of Aqueous Phase After Extraction, mg/ℓ p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	TOTAL
1.	No coalescer	1.1	1.15	2.2	0.3	4.75
2.	Glass Wool 1.5" dia x 6" deep	0.5	0.8	1.2	0.1	2.6
3.	Glass Wool + "Scotchguard" 1.5" dia x 6" deep	1.5	0.7	2.65	0.45	5.3
4.	Cotton + "Scotchguard" 1.5" dia x 6" deep	3.4	1.8	7.2	0.9	13.3
5.	Cotton 1.5" dia x 6" deep	1.5	1.0	2.2	0.2	4.9
6.	Fritted glass	0.7	0.45	1.6	0.1	2.85

In the next series, the effect of mixing time was examined. The 4:1 ratio of waste-to-MCB extractant was maintained, and the homogenizer was run at 10,000 RPM. The coalescer consisted of "Scotchguard"-coated glass wool in a 1-3/4 inch diameter tube. The results of the analyses of the aqueous extracted waste are as follows:

TABLE 30

ROSS IN-LINE HOMOGENIZER OPERATION - EFFECT OF MIXING TIME ON EXTRACTION

Mixing Time Minutes	Analyses of Extracted Aqueous Waste, mg/ℓ				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1	0.7	0.45	1.4	0.3	2.85
5	0.35	0.1	1.0	0.15	1.6
10	2.0	0.6	3.2	0.4	6.2
20	0.7	0.25	2.0	0.4	3.35

In this test, using a small coalescing mat, clear separation of the solvent and aqueous phases was not obtained. Although the results are scattered, it appears that the amount of pesticides remaining in the aqueous waste tends to increase with longer mixing times; this result agrees with earlier data where apparently a more stable emulsion tends to form as the mixing time is increased.

It has also been observed that the flow rate through the coalescer is slow, especially when the glass wool is coated with the hydrophobic silicone coating. A test was then carried out in which a small applied pressure (0-10 psi) was placed on the coalescer to increase the rate of flow through it since the non-pressurized flow rate was very low. In this test, the 4:1 waste:MCB extractant ratio and 10,000 RPM mixing speed were maintained for a five-minute mix time, and the coalescer consisted of a 10g glass wool mat coated with "Scotchguard" in a 2 inch tube. The test conditions and test results are shown in Table 31.

TABLE 31

ROSS IN-LINE HOMOGENIZER OPERATION -
PRESSURE-AIDED FLOW THROUGH COALESCER

	COALESCER TESTS			
	Coalescer	Retention Time in Coalescer	Observation*	Extraction Efficiency, %
1.	No coalescer	--	Two layers but no clear MCB layer	79
2.	Glass Wool + "Scotchguard" No applied pressure	~ 3 hrs	Two layers formed, yellow MCB layer	78
3.	Glass Wool + "Scotchguard" Max. pressure	~ 20 min	Three layers formed with yellow MCB layer	85
4.	Same as 3. at less pressure	~ 35 min	Same as 3.	63

*The suspended solids sometimes appeared to form a separate layer so that it appeared that three layers were formed.

(continued)

TABLE 31 (Continued)

Coalescer	Analysis of Extracted Aqueous Waste, mg/ℓ p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1. No coalescer	2.0	1.0	7.5	0.5	11.0
2. Glass Wool + "Scotchguard" No applied pressure	2.0	1.0	7.5	1.0	11.5
3. Glass Wool + "Scotchguard" Max. pressure	1.0	1.0	5.5	0.5	8.0
4. Same as 3. at less pressure	3.5	1.5	13.0	1.5	19.5

There does not appear to be a clear correlation between retention time in the coalescer and extraction efficiency. Since the same coalescer was used, but the applied pressure varied, the effect of reduced efficiency of extraction during the later runs may be due to increased solids deposited in the coalescer.

The effect of a second stage extraction on these samples was examined by further extracting the aqueous layer after hand mixing. The same 4:1 ratio of waste to MCB was employed. The results indicate a further reduction in toxicant values. The test conditions and test results are shown in Table 32.

TABLE 32

ROSS IN-LINE HOMOGENIZER OPERATION
"SECOND-STAGE" EXTRACTION OF HOMOGENIZER - EXTRACTED WASTE

Coalescer	Analysis of Extracted Aqueous Waste After Second Extraction, mg/l				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1. No coalescer	0.5	1.0	1.0	0.5	3.0
2. Coated Glass Wool, no pressure	1.5	1.0	5.0	0.5	8.0
3. Coated Glass Wool, max. pressure	1.5	1.5	5.5	0.5	9.0
4. Coated Glass Wool, red. pressure	14.5	4.0	20.5	2.0	41.0

(continued)

TABLE 32 (Continued)

Coalescer	Analysis of Extracted Aqueous Waste After Third Extraction, mg/ℓ				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1. No coalescer	1.5	1.0	2.5	0.5	4.5
2. Coated Glass Wool, no pressure	1.0	0.5	1.5	0.1	3.1
3. Coated Glass Wool, max. pressure	1.0	0.5	1.0	0.1	2.6
4. Coated Glass Wool, red. pressure	1.0	1.0	3.5	0.45	5.95

While some improvement was shown, a high correction for the toxicants in the MCB made precise determinations difficult; the MCB contained ~90 mg/ℓ of DDT + DDD + DDE. The tests were terminated with that source of MCB and a new lot analyzing ~3.3 mg/ℓ (DDT+DDD+DDE) was obtained from Montrose; the contaminated drum of MCB was used in this test only.

In the next series of tests, a coalescer consisting of a 3 inch diameter glass column packed about 18 inches deep with glass wool treated with "Scotchguard" hydrophobic coating was used. Flow through the coalescer was aided with a small applied pressure. The rate of rotation of the homogenizer was varied, as well as the flow rate through the homogenizer and coalescer. Good to poor extraction was achieved. The results of the test are shown in Table 33.

TABLE 33

OPERATION OF ROSS IN-LINE HOMOGENIZER
EFFECT OF HOMOGENIZER SPEED OF ROTATION ON EXTRACTION
SILICONE-TREATED GLASS WOOL COALESCER

(3 inch dia x 18 inch deep) EXTRACTOR TEST DATA

Rotation RPM	Flow Waste Ratio MCB	Flow Rate mℓ/min	Coalescer Pressure psi	Analysis of Aqueous Phase, mg/ℓ p,p' DDT	o,p' DDT	p,p' DDE	o,p' DDE	TOTAL
6,000	5.7	513	0-6	19.0	4.0	39.5	5.0	67.5
9,000	4.0	319	0-8	18.0	2.5	31.0	2.5	54.0
9,000	4.0	~300	0-6	4.0	1.0	16.0	1.5	22.5
10,000	5.15	299	0-6	18.0	5.0	20.5	2.0	45.5
10,000*	2.00	440	0-6	~0	~0	1.5	~0	1.5
10,000*	4.00	440	0-6	4.0	~0	5.0	1.0	10.0
3,000-6,000	2.81	242	0-6	2.0	~0	3.5	0.5	6.0

*Coalescer depth increased from 18 to 24 inches.

In all tests, the MCB layer was colored (yellow). At the highest speed (10,000 RPM), and the lowest ratio of waste volume to MCB volume (2.0), good separation of the pesticides was obtained. An increased depth of the coalescer also appeared to increase the extraction. This is probably a strong function of the effectiveness of phase separation, and that the apparently poor separations may be in fact MCB (laden with DDT, DDD and DDE) suspended in the aqueous layer.

The effect of mixing speed and emulsion strength was further demonstrated in a series in which 1.5 ℓ of a 3:1 waste-MCB mixture were treated for 1.5 minutes in the Ross In-line homogenizer, passed through the same coalescer as shown in Table 33, and the volume of the MCB layer measured. Both hold-up of the MCB in water, and water in MCB demonstrate a trend with mixing speed. The volume of MCB should be 375 mℓ. The results of the tests are shown in Table 34.

TABLE 34

OPERATION OF ROSS IN-LINE HOMOGENIZER - MCB RECOVERED WHEN 375 mℓ MIXED WITH WASTE AND PASSED THROUGH COALESCER

Mixer Speed, RPM	Volume of Organic Phase Separating After Mixing, mℓ
10,000	100
8,000	350
7,000	375
6,000	400
5,000	500

It is thus seen that at speeds of 6,000 to 8,000 RPM, the volume of extractant separated is approximately correct, but at higher or lower speeds, large deviations occur.

The time of mixing was examined in an experiment in which a 3:1 ratio of waste to MCB extractant was mixed at 7,000 RPM. The rate of separation of the mixture is also given. The results of the test are shown in Table 35.

TABLE 35

EFFECT OF MIXING TIME ON THE EXTRACTION WITH ROSS IN-LINE HOMOGENIZER

Mixing Time Min	Phase Separation Rate mℓ/min	Analysis of Extracted Aqueous Phase, mg/ℓ				
		p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1	105	3.0	2.0	9.5	1.5	16.0
2	73	0.5	0.5	2.0	0.05	3.0
4	38	0.1	0.2	0.5	0.1	0.9
10	22	0.5	0.5	1.5	0	2.5

While the best extraction was obtained after four-minute mixing, a substantially higher phase separation rate was observed after two-minute mixing.

A similar test (identical conditions, four-minute mixing time) was next carried out with the flow through the coalescer aided by 10 psi applied pressure. Both "Scotchguard"-coated and untreated glass wool coalescers were examined. The analysis is as shown in Table 36.

TABLE 36

OPERATION OF ROSS IN-LINE HOMOGENIZER
TESTS WITH PRESSURE-AIDED (10 psi) FLOW THROUGH COALESCER

Coalescer	Flow Rate, mℓ/min	Analysis of Extracted Aqueous Effluent, mg/ℓ				Total
		p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	
Glass Wool + "Scotchguard"	128	2.5	1.5	8.0	1.5	13.5
Untreated Glass Wool	173	9.5	3.5	19.0	2.5	34.5

In the period of a 1.5 ℓ test, the coalescer appeared to be essentially filled with suspended matter, the pressure drop increased and the coalescer became ineffective from the sludge loading.

Since the operation of the coalescer appears to involve exposure to a relatively high surface area to promote phase separation, the use of sand or fine gravel beds as a low cost, expendable coalescer was examined. The comparison was made with glass wool beds. The flow rate is for gravity flow through the bed. Some of the results are as shown in Table 37.

TABLE 37

OPERATION OF ROSS IN-LINE HOMOGENIZER
EVALUATION OF SAND AND GRAVEL AS COALESCERS

Coalescer	Coalescer Size, cm	Flow Rate ml/min	Analyses of Extracted Aqueous Effluent, mg/l				
			p,p'-DDT	o,'-DDT	p,p'-DDE	o,p'-DDE	Total
Untreated glass wool	2.5x15	3.7	~0	~0	1.0	~0	1.0
Silanized glass wool	2.5x15	5.1	~0	0.45	1.5	0.3	2.25
Sand	2.5x15	1.6	~0	~0	0.5	~0	0.5
Fine gravel	2.5x15	8.0	~0	~0	1.5	0.15	1.65
Untreated glass wool	7.5x60	40.0	~0	~0	1.0	0.15	1.65

Good promise was shown by both the sand and fine gravel in this test. Therefore, a scale-up was made of the coalescer in which a 7-1/4 inch diameter x 6 inch deep bed of fine gravel was employed. However, a clear phase separation was not obtained. Several of the samples were then centrifuged, and upon analysis of the aqueous phase, no detectable amount of DDT (either p,p'- or o,p'-) was found, although 3.5 to 4.0 mg/ p,p'-DDE and 0.2 to 1.0 mg/ℓ o,p'-DDE was detected. The MCB content of the centrifuged aqueous extracts was 577 to 949 (average 831) mg/ℓ, while the unextracted waste analyzed 413 mg/ℓ MCB (MCB solubility in water is 382 mg/ℓ, Reference 6). This level of MCB (dissolved + suspended/emulsified) is not acceptable in a treated waste.

The efficacy of the fine gravel coalescer was further checked in a test in which 21 ℓ was passed through the coalescer at a flow rate of 100 mℓ/min, and the later samples were analyzed before and after centrifuging. The results are as shown in Table 38.

TABLE 38

OPERATION OF ROSS IN-LINE HOMOGENIZER
EVALUATION OF FINE GRAVEL COALESCER

Effluent, ℓ	Analyses of Extracted Aqueous Effluent Samples mg/ℓ Before Centrifuging p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
18	1.5	1.0	9.5	1.0	13.0
19	1.5	1.0	6.0	1.0	9.5
20	2.0	1.0	9.0	1.0	13.0
21	1.5	1.0	7.5	1.0	11.0
	After Centrifuging				
18	0.15	0.15	1.5	0.1	1.9
19	0.04	0.15	1.5	0.1	1.79
20	0.15	0.15	1.0	0.2	1.50
21	0.40	0.25	2.0	0.2	2.85

A test has also been made in which sand was treated with a silicone "waterproofing" agent.* A 20 mesh silica sand was treated with the silicone, dried and formed into a 2 inch diameter x 30 inch deep coalescer bed. The homogenizer was operated at 7000 RPM and a 2 minute mixing time was employed. The results of some assays of the aqueous layer are shown in Table 39.

TABLE 39

OPERATION OF ROSS IN-LINE HOMOGENIZER
EVALUATION OF SILICONE-TREATED SAND COALESCER

	Analyses of Extracted Aqueous Effluent,**mg/ℓ					
Effluent,ℓ	MCB	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1	260	3.0	1.5	7.5	1.0	13.0
2	590	1.5	1.0	5.0	1.0	8.5
4	1270	1.0	0.5	3.5	0.5	5.5
6	1460	1.5	0.5	4.5	0.5	7.0
8	1740	1.5	0.5	4.0	0.5	6.5
10	1740	1.5	0.5	5.0	0.5	7.5
15	4320	1.5	0.5	4.5	0.5	7.0
19	3940	1.5	0.5	5.0	1.0	8.0

The results in Table 39 are anomalous in that the total pesticides remains essentially constant after the first liter of flow, while the MCB content of the waste increases steadily. After centrifuging, the MCB appeared to drop to a steady ~500 mg/ℓ, so the very high (3000-4000 mg/ℓ) MCB levels probably represent suspended MCB not separated by the coalescer.

A five minute centrifuging of some of the samples resulted in an approximate 2 mg/ℓ decrease in the total pesticides; these results suggest that DDT-DDE-laden MCB is suspended in the aqueous phase and has not been fully coalesced.

* 3M silicone FC-857; a silicone in trichloroethylene.

**Non-centrifuged

The aqueous fractions have also been analyzed for MCB content, and as the results in the table show, the solvent content of the aqueous phase increases gradually to ~4000 mg/ℓ MCB.

Further tests were made with the uncoated Pyrex glass wool coalescer. In these tests the homogenizer was operated at about 7000 RPM, and the solution flowing out of the homogenizer was passed through a 1 inch diameter x 6 inch deep glass wool bed. A waste-to-solvent ratio of 4.0 was used. The results of samples are shown in Table 40.

TABLE 40

OPERATION OF ROSS IN-LINE HOMOGENIZER
TESTS WITH GLASS WOOL COALESCER

Effluent, mℓ	MCB	Analyses of Aqueous Phase, mg/ℓ				
		p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
100	2600	--	--	1.5	--	1.5
200	1340	0.2	0.15	1.5	0.3	2.15
300	1380	0.15	0.15	2.5	0.45	3.25
400	1080	--	--	0.5	0.1	0.60

The inconsistent DDT, DDE values, and the excessive MCB in the aqueous phase suggested that a larger coalescer may be required. Further tests were made then with a 3 inch diameter x 30 inch deep glass wool packed coalescer. Other variables remained the same. The results of the test are as shown in Table 41.

TABLE 41

OPERATION OF ROSS IN-LINE HOMOGENIZER
TESTS WITH 3 INCH DIA x 30 INCH DEEP GLASS WOOL COALESCER

Effluent, ℓ	Analyses of Aqueous Phase, mg/ℓ					
	MCB	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
0.75	585	6.5	2.5	13.0	2.0	24.0
2	3200	1.5	0.5	4.5	1.5	7.5
4	2400	1.0	0.5	2.5	0.5	4.5
6	1070	0.1	0.1	0.5	0.1	0.8
8	1170	--	0.1	0.45	--	0.55

The larger coalescer gave improved effluent quality as the flow continued. This test was repeated, with a faster flow through the coalescer bed; this was accomplished by applying a 2.5 psi pressure to the coalescer, rather than the gravity feed employed in the preceding test. The flow through the coalescer increased from an average 14.5 mℓ/min in the Table 41 test to 79 mℓ/min for the data in Table 42 as shown below.

TABLE 42

OPERATION OF ROSS IN-LINE HOMOGENIZER
TESTS WITH PRESSURE-AIDED FLOW
THROUGH GLASS WOOL COALESCER

Effluent, ℓ	Analyses of Aqueous Phase, mg/ℓ					
	MCB	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
3	900	0.5	1.5	2.0	0.5	4.5
6	1740	1.0	1.5	1.5	0.45	4.45
9	1670	1.0	1.0	1.5	0.2	3.7
12	1760	1.5	1.0	4.0	0.5	7.0
15	870	0.5	0.5	2.5	0.1	3.6

Clearly, the increase in flow rate with the applied pressure on the coalescer resulted in a deterioration of coalescer performance and raffinate quality, compared with the results of Table 41.

The aqueous effluent samples from the experiments in Table 42 were reextracted with MCB solvent in order to determine whether a "second-stage" extraction similar to the initial extraction was useful. The same conditions were employed as used in the preceding test. The results are as shown in Table 43.

TABLE 43

OPERATION OF ROSS IN-LINE HOMOGENIZER
SECOND EXTRACTION OF WASTE WITH HOMOGENIZER

	Analyses of Aqueous Phase, mg/ℓ					
Effluent, ℓ	MCB	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
3	790	0.5	0.5	2.5	0.15	3.65
6	1590	--	0.25	0.35	--	0.6
9	1980	0.2	0.25	2.5	0.1	3.05
12	3490	0.2	0.25	1.0	0.1	1.55

The results shown in Table 43 are scattered but show no significant decrease in DDT, DDE content of the waste on the second extraction. On centrifuging the same samples for five minutes and analyzing, the two DDT isomers and o,p'-DDE were absent in all four samples, and the p,p'-DDE values were respectively 2.0, 2.0, 1.5 and 1.0 mg/ℓ. These results appear to further substantiate the supposition that the apparent values for the DDT and DDE largely represent uncoalesced MCB containing DDT + DDE suspended in the aqueous phase. The MCB contents of the centrifuged samples were respectively 81, 84, 250 and 290 mg/ℓ. These are significantly lower than the values obtained with the uncentrifuged samples.

Heptane Solvent Extraction Studies

Tests were also made with the Ross In-Line homogenizer using heptane rather than MCB as the extractant. Heptane was employed as the solvent in the earlier pump-loop tests (Reference 1).

In the first of these tests, the Ross homogenizer was operated at 7000 RPM, and the waste and heptane (3 volume waste: 1 volume heptane) was flowing at 100 ml/min with a five minute mixing time. No observable emulsion formed and the separation of the phases was rapid. However, the separation of the DDT and related materials was very poor. The results are as shown in Table 44.

TABLE 44

OPERATION OF ROSS IN-LINE HOMOGENIZER
EXTRACTION OF WASTE WITH HEPTANE AT 7000 RPM

	Analysis of Aqueous Phase After Extraction mg/l				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1st fraction	65.5	28.0	63.0	18.0	174.5
2nd fraction	69.0	32.5	64.5	20.0	186.0
3rd fraction	63.5	28.5	64.5	16.5	173.0

The heptane content of the aqueous samples was 990, 1280 and 1240 mg/l, respectively. Since the solubility of n-heptane in water is about 50 mg/l, an emulsion must have been present, even though it was not visually observable.

In a similar test in which the rate of rotation of the homogenizer was increased from 7000 to 10,000 RPM, and the flow rate was increased from 100 to 154 ml/min, the effectiveness of extraction remained essentially the same. The results are as shown in Table 45.

TABLE 45

OPERATION OF ROSS IN-LINE HOMOGENIZER
EXTRACTION OF WASTE WITH HEPTANE AT 10,000 RPM

	Analysis of Aqueous Phase After Extraction, mg/ℓ				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1st fraction	23.5	14.0	32.0	8.0	77.5
2nd fraction	59.0	29.0	63.5	16.0	167.5
3rd fraction	83.0	38.5	71.5	24.0	217.0

The heptane content of the aqueous extracts was 900, 1210 and 1310 mg/ℓ, respectively.

In the next test, using heptane as the extractant, a homogenizer speed of 10,000 RPM was again used for a five minute mixing time, and the ratio of waste volume to heptane was 4:1. A trace of antifoam A* was added to decrease the foam formation and a coalescer consisting of a 3 inch diameter bed of fine gravel 16 inches deep was employed to aid phase separation. Again, the separation of phases appeared good (heptane 1000 mg/ℓ in aqueous phase). The analyses of the separated aqueous phase after three periods of operation are as shown in Table 46.

TABLE 46

OPERATION OF ROSS IN-LINE HOMOGENIZER
EXTRACTION OF WASTE WITH HEPTANE AT 10,000 RPM.
EVALUATION OF ANTIFOAM AGENT

Effluent Treatment,ℓ	Analysis of Aqueous Phase After Extraction, mg/ℓ				
	p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
1	38.0	18.0	70.0	11.0	137.0
5	11.0	7.0	24.0	4.0	46.0
9	26.0	16.0	52.0	7.0	101.0

*Dow-Corning

It was thus apparent that heptane did not offer improved separations in comparison with MCB, and work with this extractant was suspended.

C. Summary of Tests With Ross In-Line Homogenizer

The tests with the Ross appear to indicate that good separation of the DDT and homologs from the waste can potentially be achieved, but that reproducible, efficient, high-flow coalescence of the phases has not been regularly obtained.

Units such as the Ross have promise of providing effective separation with lower capital costs than the Podbielniak contactor, assuming that a compatible solvent system can be identified. The Ross can only be useful in cases where effective phase coalescence and separation are achieved. This appears to be impossible with the waste-solvent systems examined.

SECTION 6

BAFFLED STIRRERS

A. Description of Stirrer System

Another potential system for providing relatively high-shear stirring involves the use of turbine-type stirrers in a baffled tank. This concept was examined using the Bench-Scale Equipment system. The experimental set-up consisted of a seven-gallon glass tank fitted with four vertical, adjustable baffles. Stirring was achieved with 3 inch diameter turbine mixer blades and a 1725 RPM mixer. Three different mixer blades were employed: a straight blade turbine, a tapered blade unit and a curved blade turbine.

B. Experimental Results

In the first test, the three types of mixer blades were compared. For each test run, the seven-gallon tank contained 2 ℓ total with a volume ratio of 4.00 volume aqueous waste:1.00 volume MCB solvent.

The samples after mixing for stated periods of time were passed through a 1 inch diameter x 6 inch long coalescer filled with glass wool. The results are as shown in Table 47.

TABLE 47

EXTRACTION OF MONTROSE WASTE IN BAFFLED TANK USING STRAIGHT BLADE, CURVED BLADE AND TAPERED BLADE TURBINE STIRRERS

Mixing Time Min.	Analysis of Aqueous Phase After Extraction, mg/ℓ p,p'-DDT	o,p'-DDT	p,p'-DDT	o,p'-DDE	Total
		Straight Blade Turbine			
2	1.00	0.50	2.50	0.35	4.35
5	0.45	0.40	1.50	0.50	2.85
10	0.27	0.25	1.00	0.07	1.59
20	0.37	2.25	0.42	0.68	3.72
		Tapered Blade Turbine			
2	0.35	0.25	1.50	0.20	2.30
5	0.40	0.30	2.00	0.20	2.90
10	0.45	0.35	2.00	0.25	3.05
20	0.35	0.30	1.50	0.20	2.35
		Curved Blade Turbine			
2	0.40	0.30	2.00	0.20	2.90
5	0.35	0.20	1.50	0.20	2.25
10	0.45	0.30	2.00	0.20	2.95
20	0.50	0.40	3.00	0.30	4.25

The extraction results, based on residual pesticide content of the aqueous phase, appeared comparable for the tapered and curved blade turbines. The amount of MCB which separated in a clear layer (i.e., was not emulsified) was largest for the tapered blade mixer, and this unit was employed in further tests. It is of importance to note that a two to five minute mixing time in the single stage mixer has given extraction efficiencies comparable to the homogenizers. The above tests also show that neither mixer blade type nor mixing time significantly affect extraction efficiency.

A further test was made using the tapered blade turbine, a five minute mixing time and the 4:1 volume ratio of waste to MCB. The coalescer is this test was a 3 inch diameter x 30 inch long column of glass wool. At the

conclusion of the mixing period, the 25 ℓ sample was passed through the coalescer. Three tests were made, with the mixer-baffle clearance being varied for each test. The average results of the analysis of the aqueous fraction from each test are shown in Table 48.

TABLE 48

EFFECT OF BLADE-BAFFLE CLEARANCE
ON EXTRACTION EFFICIENCY
ANALYSIS OF AQUEOUS PHASE AFTER EXTRACTION, μg/ℓ

Component	Blade-Baffle Clearance, in. 3.30	2.20	1.50
p,p'-DDT	0.54	0.30	0.16
o,p'-DDT	0.46	0.26	0.11
p,p'-DDE	2.10	1.21	0.69
o,p'-DDE	0.35	0.22	0.08
TOTAL	3.45	1.99	1.04
Flow through Coalescer ml/min	131	88	78

The results in Table 48 show improved extraction as a function of lower flow rate through the coalescer and as a function of decreased blade-baffle clearance (producing greater shear).

A possible method for utilizing the baffled stirred vessel system could involve multiple stirred baths with countercurrent flow of the aqueous waste and MCB extractant. With this in mind, an experiment was set up to examine this concept. A single batch of aqueous waste was extracted three times with fresh solvents. In this test, the tapered blade turbine stirrer was employed with a 4:1 ratio of waste-to-MCB solvent. The mixing time was five minutes, and the mixed phases were passed through a 3 inch diameter x 42 inch deep bed of glass wool to coalesce the phases. The results of the test are as shown in Table 49.

TABLE 49

MULTIPLE EXTRACTION OF MONTROSE WASTE
WITH BAFFLED STRAIGHT-BLADE TURBINE MIXER

Volume, ℓ	MCB	Analysis of Aqueous Phase After Coalescense, mg/ℓ p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
			1st Extraction			
5	1140	1.50	1.0	4.5	0.50	7.5
10	510	1.50	1.0	4.5	0.50	7.5
15	250	0.50	0.5	2.0	0.20	3.2
20	710	0.50	0.5	2.0	0.50	3.5
25	810	0.50	0.5	2.5	0.50	4.0
30	880	0.20	0.2	1.0	0.10	1.5
35	540	0.25	0.2	1.0	0.15	1.6
			2nd Extraction			
5	680	0.05	0.05	0.50	0.05	0.65
10	570	0.15	0.15	0.50	0.10	0.90
15	440	0.05	0.05	0.25	0.025	0.375
20	440	0.04	0.04	0.25	0.013	0.363
			3rd Extraction			
5	450	0.025	0.025	0.083	0.025	0.158
10	340	0.033	0.033	0.167	0.017	0.270
14	330	0.033	0.042	0.083	0.017	0.175

Samples were analyzed after each 1 ℓ effluent, and the average of these date indicates a 95.4% extraction after the first extraction, 99.5% after two extractions and 99.7% removal after three extractions. The averages of the fourteen 1 ℓ sample analyses after three extractions were 0.033 mg/ℓ p,p'-DDT, 0.042 mg/ℓ o,p'-DDT, 0.083 mg/ℓ p,p'-DDE and 0.017 mg/ℓ o,p'-DDE, giving a total of 0.175 mg/ℓ. The average MCB content of the aqueous fraction was 381 mg/ℓ, which is almost identical with the published solubility of MCB (382 mg/ℓ, Reference 6).

C. Summary of Baffled Stirrer Tests

The baffled stirrer in a countercurrent multiple extraction arrangement appears to give good extraction, ranging from 95.4% after one extraction to 99.7% after three extractions. The material appears to coalesce well and the phases separate readily. The MCB in the aqueous phase is substantially lower than with the homogenizer tests.

SECTION 7

OTHER MIXING SYSTEMS

Several mixers were evaluated to a lesser degree in the course of the studies. These include the Ross and Polytron homogenizers and a Waring blendor.

A. Waring Blendor

An early screening test was made with the Waring blendor as an example of a very high-shear rate mixer. The undiluted waste and MCB were mixed (ratio 3 volumes waste to 2 volumes MCB in the blendor. A marked rise in temperature was noted, and the phases did not readily separate after mixing. The temperature of the mix as a function of mix time are as shown in Table 50.

TABLE 50

TEMPERATURE OF WASTE-MCB MIX
AS FUNCTION OF MIX TIME IN WARING BLENDOR

Mixing Time, Min	Temperature, °C
0	25
1	28
2	38
5	40
10	41
20	41
30	55
45	58
60	62

The poor separation of phases was traced in part to the finding that the MCB and aqueous waste have virtually identical densities (waste 1.10 g/mℓ, MCB 1.098 g/mℓ) so that gravity separation is poor. Following this finding, the aqueous wastes have been diluted with water so that a reasonable density difference exists between the waste and solvent phases. The tests with the Waring did not give good separations because of the very high-shear mixing tended to form stable emulsions, and the tests were discontinued as soon as the Ross laboratory homogenizer was obtained.

B. Ross Laboratory Homogenizer

Tests were also made with a Ross laboratory homogenizer while awaiting the delivery of the in-line model. These tests gave an indication that high shear velocities were required to give good separation, that a short (~2 min) time was needed, and that an adequate coalescer was needed. In an early test, for example, a 9000 RPM velocity was used with gravity separation of the phases. These results show about 20 mg/ℓ p,p'-DDE and 10 - 12 mg/ℓ of the o,p'-isomer while the p,p'-DDT was 3 - 4 mg/ℓ and the o,p'-DDT 1 - 2 mg/ℓ. Tests with heptane as solvent led to a jelly-like phase. In a comparison of coalescers, glass frit was better than overnight standing for phase separation. A glass wool mat was also effective.

C. Polytron Homogenizer

The Polytron, a homogenizer produced by Brinkman Instruments, was also evaluated. This device consists of two sets of closely fitting cutting blades rotating in opposite directions at high rates of speed. This device is available in an in-line model similar to the Ross. The speed of rotation of the Brinkman may be varied up to 20,000 RPM, while the Ross is variable up to 10,000 RPM. A series of qualitative runs were made to determine whether separable phases were formed, and on mixing water and MCB it was found that at the higher mixing speeds, very stable emulsions were formed. In a series of tests, 375 mℓ of MCB was mixed for 1.5 minutes with 1125 mℓ of the aqueous waste, the solution passed through the given coalescer, and the amount of MCB which separated was noted. The layers were then analyzed for DDT, DDD and DDE. The results are as shown in Table 51.

TABLE 51

EXTRACTION TESTS WITH BRINKMAN POLYTRON HOMOGENIZER

RPM	Coalescer	MCB Recovered mℓ	Analysis, mg/ℓ p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
22,000	Glass Wool	50	2.0	1.5	6.0	4.0	13.5
22,000	Glass Wool + "Scotchguard"	50	0.5	0.5	5.5	0.5	7.0
10,000	Glass Wool	275	6.5	1.5	16.0	1.5	25.5
16,000	Glass Wool	150	4.0	1.0	11.0	1.0	17.0

These results document the previously stated conclusion that at the highest speeds, much of the MCB is formed into a stable emulsion, while at lower speeds of rotation the extraction is not as efficient. The evaluation of the Polytron was terminated with these results, as the system appeared to offer no advantage over the Ross.

SECTION 8

CHEMICAL REDUCTION OF RESIDUAL MONOCHLORBENZENE IN THE AQUEOUS EXTRACTS

The earlier tests have shown that the aqueous waste, either before or after extraction, contains a few hundred to a few thousand mg/ℓ of monochlorbenzene (MCB). These levels are too high to permit dumping a treated waste in a municipal sewer system. A limited evaluation was carried out to determine the feasibility of removing the MCB by the Envirogenics reductive degradation process.

A reduction column was prepared by mixing 600 g of catalyzed iron powder with 2150 g of 30 mesh sand and placing the blend in a 3.7 cm diameter column to a depth of 165 cm. The aqueous MCB emulsion was allowed to flow through the bed at an average (low) flow rate of 15.6 m /min (0.36 GPM/sq ft). In the first test, a 79 mg/ℓ MCB solution was passed through the column four times. The MCB analysis after the first pass was 48.1 mg/ℓ, 30 mg/ℓ after the second pass, 20 mg/ℓ after the third pass and 11 mg/ℓ after the fourth pass.

In the second test, a 225 mg/ℓ aqueous MCB solution was passed through the column six times. The assay after each pass was as follows: 1st - 154 mg/ℓ, 2nd - 97 mg/ℓ, 3rd - 58 mg/ℓ, 4th - 39 mgℓ, 5th - 28 mg/ℓ and 6th - 22 mg/ℓ. These data indicate an 86% degradation of MCB after four passes in the first test, and a 90.2% degradation after six passes in the second test. Cyclohexanol was shown to be a reduction product, on the basis of chromatography of derivatives, and comparison with authentic cyclohexanol.

In another test, an extracted Montrose waste from a baffled stirrer experiment (Section 6) was also passed through the column. The results of the test are as shown in Table 52.

TABLE 52

ANALYSIS FOR MONOCHLORBENZENE
DDT AND DDE AFTER TREATMENT IN REDUCTION COLUMN

Sample	MCB	Analysis of Aqueous Phase, mg/ℓ				
		p,p'-DDT	o,p'-DDT	p,p'-DDE	o,p'-DDE	Total
Initial	641	0.20	0.20	1.00	0.15	1.55
1st Column Pass	427	0.20	0.31	1.25	0.19	1.95
2nd Column Pass	163	0.12	0.32	0.83	0.13	1.40
3rd Column Pass	128	0.20	0.25	1.25	0.15	1.85
4th Column Pass	90	0.15	0.20	1.50	0.15	2.00

While a gradual decrease is shown in the MCB content of the waste, there appears to be no significant change in DDT or DDE level of the waste. Earlier studies (Reference 1) show that DDT can be reduced, though DDE can only be reduced under extreme conditions.

SECTION 9

ANALYSIS OF RESULTS

The treatment of the alkaline waste liquor from DDT manufacturing operations is a complex problem requiring the solution of several problems. Important are the following considerations:

- Effective removal of DDT, DDD and DDE
- Environmental effect of other components in the waste and their treatment if necessary
- The ultimate disposal of the DDT and metabolites, including a suitable degradation process if necessary
- The capital and operating cost of a suitable process to dispose of the waste

Each of these problems can be discussed separately in this section.

The concept of efficient extraction of the DDT and DDE from aqueous alkaline DDT manufacturing waste appears to have been demonstrated in principle by the results of at least three mixing techniques. Reduction of the DDT + DDE levels (both p,p'- and o,p'-isomers) to of the order of 2 mg/ℓ has been shown for both the Podbielniak continuous contactor and the Ross continuous homogenizer, when operated at flow rates of the order of 1 ℓ/min. A three stage countercurrent mixer using a turbine mixer in baffled tanks was able to reduce the DDT + DDE level to about 0.2 mg/m . However, an important problem remains. It is particularly evident with the homogenizer results, but also evident to a lesser degree with the Podbielniak and baffled stirrer results, that adequate coalescence of the phases and effective separation of the aqueous phase from the solvent has not been effectively and reproducibly shown. The substantial reduction of the DDT and DDE in samples which have been centrifuged provides evidence that the residual DDT (+ DDE) may, to a large extent, be dissolved in MCB suspended in the aqueous phase.

A "second-stage" extraction, particularly with the Podbielniak system, appeared capable of reducing the DDT, DDE levels significantly, with the DDT generally being at or below detection levels, and the DDE 0.1 mg/ℓ or less. A simple packed tower extraction would appear adequate for this step since the high-shear mixing in the first stage would serve to free the DDT, DDE from carbonaceous particles with which it may be associated in the waste.

Extraction with monochlorbenzene (MCB) appears to be better than with the hydrocarbon solvent heptane (used in the earlier Contract 68-01-0083 studies, Reference 1), and MCB would be preferred on the basis of reduced flammability and simpler disposal of the extracted DDT, DDE. It should be noted, though, that dilution of the waste with water is necessary so that there is sufficient density difference between the waste and MCB to allow phase separation.

In view of the fact that solvent extraction does not appear to be an acceptable alternative to present practice, there is no point in attempting to estimate process costs. It is obvious that the severe coalesence problems would require considerable time to solve. If long holding times are necessary to provide for phase separation, tanks become unacceptably large, and the process becomes unacceptably expensive.

Another area of concern is the ultimate disposal of the extracted DDT and DDE. As discussed earlier, it was hoped that the use of MCB as an extractant would allow the MCB to be recycled to the condensation step. Since it would appear that MCB cannot be used as a solvent due to excessive solvent loss, then the recycle advantage is lost. If another solvent were identified which were ideal as an extractant, it could not be recycled to the DDT synthesis process. An alternative final disposal system would be necessary for the pesticide-laden solvent.

In summary, the effective extraction of DDT and metabolites by the continuous high-shear mixing system has been investigated, with effluent levels of ~2 mg/ℓ DDT + DDE being shown for the Ross homogenizer and Podbielniak contactor, and as low as 0.2 mg/ℓ for a three-stage baffled stirrer. Further extraction to remove the residual DDT and DDE to ~0.1 mg/ℓ has been shown also. However, adequate coalescence of the phases remains a problem.

The January 12, 1977, Federal Register prohibits any discharge of DDT from the manufacturing process for either new or existing sources. The ambient water criterion for DDT in navigable water is 0.001 $\mu g/\ell$ or 0.001 parts per billion.

Although the one existing DDT manufacturing plant would discharge to a line feeding a county sewage treatment plant, and not to navigable water, it is clear that the technology tested under this grant is incapable of generating waste which will meet the provisions of the toxic pollutant standard. The current operation of this plant does meet the toxic pollutant standard. There would appear to be no alternative to the present disposal practice which consists of placing the caustic waste in a Class I landfill.

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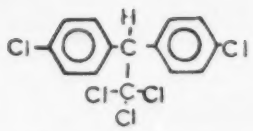
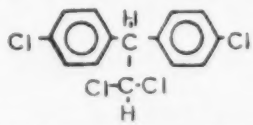
GLOSSARY

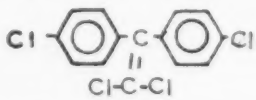
CHEMICAL FORMULAS OF PESTICIDES AND DEGRADATION PRODUCTS

DDT 

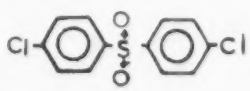
2, 2 bis(p-chlorophenyl)-1, 1, 1-trichloroethane

DDD (TDE) 

2, 2 bis(p-chlorophenyl)-1, 1-dichloroethane

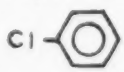
DDE 

2, 2 bis(p-chlorophenyl)-1, 1-dichloroethylene



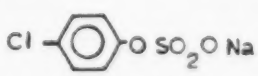
DDS

bis(p-chlorophenyl)sulfone

MCB 

(mono)chlorobenzene

NaMCBS



Sodium p-chlorobenzene sulfonate

GLOSSARY (Continued)

SOLUBILITY OF PESTICIDES AND DEGRADATION PRODUCTS IN WATER

Material	Solubility	Reference
DDT	14 refs ranging in sol to 1 ppm 1-3 ppb most probable	5
DDD	Insol, negligible	5
DDE	----	
DDS	----	
MCB	0.0382% (25.2°C) 488 mg/ℓ (30 °C)	6
NaMCBS	15.21% (25 °C)	6

CONVERSION UNITS

Gallon	3.78
Inch	2.54 cm
Pounds per square inch (psi)	0.070 kg/cm^2